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(19)

(54) PRESSURE-SENSITIVE ADHESIVE

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to mixtures of an ethylene copolymer and a natural or synthetic resin as pressure-sensitive adhesives.

Prior art pressure-sensitive adhesives consist of a mixture of an ethylene/vinyl acetate copolymer and a tackifier such as rosin or terpene resins. In most cases, the compatibility of the ethylene/vinyl acetate copolymer with the tackifiers is unsatisfactory. Further drawbacks of these mixtures are their inadequate heat resistance and unsatisfactory cohesion. Other mixtures are known which consist of an ethylene/ethyl acrylate copolymer or an ethylene/butyl acrylate copolymer and a tackifier. These mixtures are used as hot-melt adhesives. Their surface is non-tacky or only slightly tacky at room temperature, and they cannot therefore be used as pressure-sensitive adhesives. Another drawback of these mixtures is their inadequate compatibility with tackifier resins.

The present invention seeks to provide pressure-sensitive adhesives having high thermal stability and cohesion and containing components showing a high degree of compatibility with each other and remaining in admixture with each other without separation even when heated for relatively long periods.

The invention provides a pressure-sensitive adhesive containing a mixture of from 80 to 30% by weight of an ethylene copolymer which contains from 25 to 50% by weight of polymerized units of methyl acrylate and has a melt index of from 10 to 100 g/10 min., and from 20 to 70% by weight of a tackifier resin.

Copolymers of ethylene and methyl acrylate may be prepared by copolymerization of ethylene with methyl acrylate at pressures above 500 atmospheres and temperatures of from 150° to 400°C in the presence of free-radical polymerization initiators. Suitable ethylene/methyl acrylate copolymers for the manufacture of pressure-sensitive adhesives contain from 25 to 50% of methyl acrylate in the form of polymerized units and have a melt index of from 10 to 100 g/10 min. (as measured at a temperature of 190°C and under a load of 2.16 kg according to ASTM D 1238/65 T).

The ethylene/methyl acrylate copolymer is mixed in accordance with the invention with a tackifier resin. Suitable tackifier resins are natural resins, modified natural resins and synthetic resins. These tackifiers are solid, amorphous, hard to brittle, thermoplastic substances which generally soften at temperatures of from 40° to 140°C and generally have molecular weights or average molecular weights of from 200 to 7,000.

Suitable natural resins and modified natural resins are, for example, terpene resins (also known as polyterpene resins), balsam resins, rosin, hydrogenated rosin, esters of rosin or hydrogenated rosin, for example glycerol esters, pentaerythritol esters, ethylene glycol esters, diethylene glycol esters, triethylene glycol esters, propyl esters and methyl esters of rosin or hydrogenated rosin. The hydroabietyl alcohol resulting from complete hydrogenation of rosin may also be used in esterified form. For example, the acid ingredient may be benzoic or phthalic acid. Other good tackifiers are conventional terpene and alkylphenol resins and also synthetic resins such as ketone resins, hydrocarbon resins, e.g. cumarone resins, in-

dene resins and hydrocarbon resins obtained from petroleum, styrene copolymers obtained, for example, by polymerization of vinyl toluene and styrene or isobutylene and styrene. Another suitable tackifier is polyisobutylene having a molecular weight of from 1,000 to 50,000 (determined by the Staudinger method).

We prefer to use those resins which contain a minimum of acid groups and have an acid number of less than 100, preferably of from 0 to 200. It may be advantageous to use mixtures of more than one tackifier, for example mixtures of from 2 to 4 different resins. Where use is made of mixtures of resins having different softening points, for example a mixture of resin having a softening range near 70°C and resins having a softening range near 120°C, the resulting pressure-sensitive adhesive may be used over a greater temperature range than an adhesive containing only one resin.

The mixtures may be prepared in conventional equipment, for example in kneaders, extruders or stirred vessels. The components may, if desired, be mixed in the presence of a solvent. Suitable solvents are aromatic and chlorinated hydrocarbons such as benzene, toluene, xylene, chlorobenzene, methylene chloride and chloroform. The mixtures may contain additives such as are normally added to ethylene copolymers, for example stabilizers, aging retardants, dyes, pigments and waxes.

The mixture of ethylene/methyl acrylate copolymer and tackifier may be applied to a base, for example by extrusion or roller-application or by means of casting machines. If application is made from the melt, it will be necessary to heat the mixture to temperatures of from about 120° to 250°C. Alternatively, the mixture may be applied to a base from solution at room temperature, in which case the solvent must be removed after application.

Suitable bases for the above pressure-sensitive adhesives are for example paper, textile fabrics of synthetic or natural fibers, nonwovens, wood, rubber, metal, glass, cast bitumen, bitumenized cardboard and plastics sheet or film. For example, the pressure-sensitive adhesives may be applied to paper or film of polyethylene, polypropylene, polyvinyl chloride, polyethylene glycol terephthalate or polystyrene. When applying the adhesives to heat-sensitive film, use may be made of the transfer process, i.e. the adhesive is first applied to silicone paper to form a coating thereon which, after cooling, is transferred to the heat-sensitive film. The melt viscosity of the pressure-sensitive adhesive without solvent is normally from 5,000 to 100,000 centipoise at a temperature of 180°C.

The above pressure-sensitive adhesives are suitable for the manufacture of self-adhesive materials such as self-adhesive film, labels, floor coverings, wall coverings, medicinal plasters and vibration dampeners.

The invention is further described with reference to the following Examples.

In the Examples, 40 μm thick films of polyethylene glycol terephthalate are coated with a 25 μm thick layer of pressure-sensitive adhesive (corresponding to a rate of application of 25 g/m²). The adhesive may be applied in the molten state or from a solution (for example in toluene) to said polyethylene glycol terephthalate film. When a solvent is used, it is necessary to evaporate this under reduced pressure after application. During this process, the temperature of the coated film should not exceed about 130°C. To assess the adhesive properties of the film coated with the pressure-sensitive adhesive, the surface tack is determined at room temperature after drying and at a temperature of 70°C after a storage period of 7 days, the tests used being the probe-tack test and the peel strength test. In addition, the cohesion of the layer of adhesive is determined by means of the shear test.

To test the surface tack by the probe-tack test and the peeling strength test, a film coated with pressure-sensitive adhesive is cut into test strips having a width of 2 cm, these being stored, both before and after storage at 70°C, in a conditioning chamber at a temperature of 20°C and a relative humidity of 65% for 24 hours.

The probe-tack test is carried out under the following conditions using a polyken probe-tack tester as described in the Special Technical Publication No. 360 of ASTM (1963): contact time 0.2 sec., speed 2 cm/sec. and weight 20 g/cm².

In the peeling test, the 2 cm wide test strips are stuck to a chromium-plated sheet and are peeled off in a direction parallel to the adhesive layer, i.e. at an angle of 180°, the force required for this operation being measured. The speed is 300 mm/min. The measurement is carried out 24 hours after the strips have been stuck to said sheet.

The shear test is carried out in the manner described in German Published Application 2,134,688. The test strips are stuck to a highly polished chromium-plated sheet having an area of 20 × 25 mm. The sheet is clamped in a vertical position and the free end of the test strip stuck thereto is weighted with 1,000 g. The time taken for the bond to give under this constant tension is determined. The measurement is carried out at from 20 to 50°C.

EXAMPLE 1.

A 40 μm thick polyethylene glycol terephthalate film is coated with a 25 μm thick layer of a mixture of 50 parts of an ethylene/methyl acrylate copolymer and 50 parts of a hydrogenated rosin having a softening point

between 75° and 80°C. The ethylene copolymer contains 65% of ethylene and 35% of methyl acrylate, by weight. It has a melt index of 50 g/10 min. The softening point of the polymer is 93°C. The adhesive properties of the resulting pressure-sensitive adhesive film are listed in the Table below.

EXAMPLE 2.

Example is repeated except that an ethylene/methyl acrylate copolymer is used which contains 60% of ethylene and 40% of methyl acrylate, as polymerized units, by weight. The melt index of this polymer is 15 g/10 min. Its softening point is 115°C. The adhesive properties of the pressure-sensitive adhesive film are listed in the Table below.

EXAMPLE 3.

50 parts of the ethylene copolymer described in Example 1 are mixed with 50 parts of the phthalic ester of hydroabietyl alcohol having a softening point of from 60° to 70°C. The mixture is a pressure-sensitive adhesive and is applied to the film described in Example 1 in a thickness of 25 μm. There is obtained a pressure-sensitive adhesive film having the properties given in the Table below.

EXAMPLE 4.

70 parts of the ethyl/methyl acrylate copolymer described in Example 1 are mixed with 30 parts of a hydrocarbon resin having a softening range of 80—90°C. The properties of the pressure-sensitive adhesive film obtained therewith are listed in the Table.

EXAMPLE 5.

60 parts of the ethylene copolymer described in Example 1 are mixed at a temperature of about 190°C with 40 parts of a terpene-phenol resin having a softening range of from 63° to 70°C. The mixture is applied to a film of polyethylene glycol terephthalate in a thickness of 25 μm in the manner described in Example 1. There is obtained a pressure-sensitive adhesive film having the properties given in the Table below.

EXAMPLE 6.

Example 1 is repeated except that in place of a hydrogenated rosin 50 parts of the pentaerythritol ester of hydrogenated rosin are used. The tackifier softens in the range 102° to 110°C. The film described in Example 1 is coated with the resulting mixture. The thickness of the coating is 25 μm. The properties of the resulting pressure-sensitive adhesive film are given in the following Table.

EXAMPLE 7.

25 parts of an ethylene/methyl acrylate copolymer containing 67% of ethylene and 33% of methyl acrylate, by weight, and having a melt index of 50 and a softening point (determined according to Kraemer-Sarnow) of 95°C are mixed with 75 parts of an isobutylene styrene resin at a temperature of 220°C. The isobutylene/styrene resin has a softening range of from 80° to 85°C. The film described in Example 1 is coated with a 25 μm thick layer of the resulting mixture. There is obtained a pressure-sensitive adhesive film having the properties given in the Table below.

The following Table lists the pressure-sensitive films obtained according to the above Examples and the properties determined thereon.

TABLE

Ex. No.		1	2	3	4	5	6	7
Peeling strength	after 24 hrs	1220	1010	1100	810	1030	1060	1800
	after 7 days at 70°C	1310	1050	1100	850	1070	1080	1900
Probe-tack	immediately	830	550	720	400	420	700	510
	after 7 days at 70°C	670	370	640	370	410	680	570
Shear strength at 20°C								
	after 24 hrs	>3 days	>3 days	>3 days	>3 days	>3 days	>3 days	48 hrs
	after 7 days at 70°C	>3 days	>3 days	>3 days	>3 days	>3 days	>3 days	55 hrs
Shear strength at 50°C								
	after 24 hrs	50'	60'	40'	110'	60'	60'	20'
	after 7 days at 70°C	70'	75'	50'	120'	70'	65'	30'

WHAT WE CLAIM IS:—

1. A pressure-sensitive adhesive containing a mixture of from 80 to 30%, by weight of an ethylene copolymer containing from 25 to 50% by weight of polymerized units of methyl acrylate and having a melt index of from 10 to 100 g/10 min., and from 20 to 70% by weight of a tackifier resin.

2. A pressure-sensitive adhesive as claimed in claim 1, wherein the tackifier resin comprises a thermoplastic resin which softens between 40° and 140°C.

3. A pressure-sensitive adhesive as claimed in claim 1 or 2, wherein the tackifier resin comprises hydrogenated rosin, a phthalic ester of hydroabietyl alcohol, a hydrocarbon resin, a terpenephenol resin, a pentaerythritol ester of hydrogenated rosin or an isobutylene/styrene resin.

4. A pressure-sensitive adhesive as claimed in any of claims 1 to 3, wherein the resin has an acid number of less than 20.

5. A pressure-sensitive adhesive as claimed in any of claims 1 to 4, wherein a mixture of tackifier resins of different softening points is used.

6. A pressure-sensitive adhesive as claimed in claim 1 and specified in any of the foregoing Examples.

7. An adhesive product comprising a pressure-sensitive adheaive composition as defined in any of claims 1 to 6 on a base of paper .r a plastics sheet or film.

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